Near-Edge X-ray Absorption Fine-Structure Study on Hydrogenated Boron-Doped Ultrananocrystalline Diamond/Amorphous Carbon Composite Films Prepared by Coaxial Arc Plasma Deposition

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Boron-doped ultrananocrystalline diamond/amorphous carbon composite films were deposited in the hydrogen pressure range up to 26.7 Pa by coaxial arc plasma deposition with a boron-blended graphite target, and the effects of hydrogenation on the electrical properties and chemical bonding structures of the films were discussed by near-edge X-ray absorption fine structure (NEXAFS) studies. The electrical conductivity decreased with increasing hydrogen pressure. Whereas the nonhydrogenated films showed a semimetallic behavior in the temperature dependence of the electrical conductivity, the hydrogenated films exhibited semiconducting behavior. The boron content estimated from X-ray photoelectron spectroscopic measurements hardly changed with the hydrogen pressure. NEXAFS spectra showed that π* resonance related to sp²-bonded carbon is evidently enhanced with decreasing hydrogen pressure, which is accompanied by a selective etching of sp² carbon. The results indicate that the carrier transports in UNCD/a-C films are strongly influenced by chemical bonding structure at a-C or grain boundaries.

Key words: ultrananocrystalline diamond, amorphous carbon, electrical conductivity, near-edge X-ray absorption fine-structure, X-ray photoelectron spectroscopy

1. INTRODUCTION

Ultrananocrystalline diamond (UNCD)/hydrogenated amorphous carbon (a-C:H) composite (UNCD/a-C:H) films, wherein UNCD grains are embedded in an a-C:H matrix, are candidates for applications to MEMS,¹ field emission,² photodetector,³ and bio-sensing.⁴-⁵ UNCD/a-C:H films possess the following features: a) large optical absorption coefficients of more than 10⁴ cm⁻¹ in the photon energy range from 3 to 6 eV,⁶,⁷ and b) p and n-type conductions are possible by doping nitrogen and boron atoms, respectively.⁸,⁹ These characteristics might be owing to a large number of grain boundaries (GBs). Here, GBs denote the interfaces between UNCD grains and those between UNCD grains and an a-C:H matrix in the films. It has been experimentally demonstrated that heterojunction diodes comprising boron-doped UNCD/a-C:H films prepared by physical vapor deposition (PVD) such as pulsed laser deposition (PLD) and coaxial arc plasma deposition (CAPD) and n-type Si substrates exhibit a typical rectification action and photodetection for deep ultraviolet light.¹⁰,¹¹ From the rectifying action of the diodes, it was found that carriers are dominantly transported through GBs and a-C:H.¹²

Concerning boron doping for producing p-type conduction, we have reported that hydrogen atoms that terminate dangling bonds at GBs are replaced by boron atoms.⁸ In addition, it is well known atomic hydrogen preferentially etches sp² bonds during the film deposition. It is expected that hydrogen atmospheres during the deposition play important roles in the structural and electrical property of boron-doped UNCD/a-C:H films.

Nanodiamond films have mainly been prepared by chemical vapor deposition (CVD), such as hot filament CVD, microwave CVD. In the deposition by CVD, hydrogen atoms are spontaneously incorporated into the films from source and carrier gas, hence, it is difficult to discuss the effects of hydrogen incorporation on the physical and electrical properties of the films. CAPD does not necessarily need hydrogen atmospheres during the deposition for the formation of UNCD grains.¹³ Thus, the hydrogenation of the film can be adjusted by changing the hydrogen pressure during the deposition. In CAPD, hydrogen molecules gas fed into a vacuum chamber is effectively dissociated to atomic hydrogen in plasma.¹⁴

In this study, CAPD was employed for preparing hydrogenated boron-doped UNCD/a-C:H films,¹⁵ and change in the electrical properties and structures of the films for hydrogenation were investigated. Concretely, the hydrogen pressure during the film deposition was changed for adjusting the hydrogenation and the chemical bonding structures were investigated by
nondestructive spectroscopic methods with synchrotron radiation. We discuss the hydrogenation effects on the electrical properties of the films on the basis of the chemical bonding structural results.

2. EXPERIMENTAL PROCEDURE

Boron-doped UNCD/a-C:H films with a thickness of 200 nm were deposited on Si and quartz substrates in hydrogen atmospheres at a substrate temperature of 550 °C by CAPD with 5 at.% boron-blended graphite targets. The film preparation was carried out at hydrogen pressures of 0, 1.3, 6.7, and 26.7 Pa for comparison. Hydrogen gas was fed into a film preparation chamber after the chamber was evacuated down to base pressures of lower than 10⁻⁴ Pa by a turbo molecular pump. A voltage of 100 V was applied to the arc plasma gun equipped with a capacitor of 720 μF. The repetition rate of arc discharge was 5 Hz. The distance between the substrate and the front of the arc plasma gun was 15 mm.

The electrical conductivity of the films deposited on quartz substrates was measured by the van der Pauw method, and the temperature dependence of the electrical conductivity was studied in the temperature range from 250 to 500 K. Pd ohmic electrodes were deposited on the film surface by radio frequency magnetron sputtering. The existence of UNCD grains in the films was confirmed by X-ray diffraction with synchrotron radiation. The chemical bonding structures of the films deposited on Si substrates were investigated by X-ray photoelectron emission and near-edge X-ray absorption fine structure (NEXAFS) spectroscopies. X-ray photoelectron spectroscopy was performed using Mg Kα line with photon energy of 1253.6 eV as a light source. NEXAFS spectra were obtained in total electron yield (TEY) mode. Any surface treatments such as sputtering with Ar⁺ ion were not conducted before the measurements in order to prevent the films from being damaged. The boron contents in the film were estimated from the X-ray photoelectron spectra. The spectroscopic measurements with synchrotron radiation was carried out at beamline 12 of Kyushu Synchrotron Light Research Center.

3. RESULTS AND DISCUSSIONS

The electrical conductivity \( \sigma \) as a function of the inverse of temperature \( T \) is shown in Fig. 1. With increasing hydrogen pressure, the electrical conductivity evidently decreases. For the film deposited at 26.7 Pa, it was impossible for the electrical conductivity to be measured. Whereas the temperature dependence of the electrical conductivity of the 6.7-Pa film is a typical semiconducting behavior, those of the nonhydrogenated and 1.3-Pa films are semimetallic rather than semiconducting.

The activation energy can be estimated from the temperature dependence of the electrical conductivity using the following Arrhenius law:

\[
\sigma = \sigma_0 \exp \left( -\frac{E_a}{k_B T} \right)
\]

Here, \( E_a \), \( \sigma_0 \), and \( k_B \) are the activation energy, constant, which can be extrapolated from experimental data, Boltzmann constant, respectively. The gradient of the plot gradually changes with \( 1/T \), which means that the activation energy is variable for temperature. The activation energy estimated from the plot ranges from 0.005 to 0.05 eV around room temperature.

It is known that the temperature dependence of the
electrical conductivity in hopping conduction is expressed by the following equation.\(^{16}\)

\[
\sigma = \sigma_0 \exp \left( -\frac{T_o}{T} \right)^{1/4}
\]

Here, \(\sigma_0\) is a prefactor and \(T_o\) is a material-dependent constant. Figure 2 shows the plots of the electrical conductivity as a function of \((1/T)^{1/4}\). The value of \(m\) is dependent on the transport mechanism of carriers as follows. The value of 1 means nearest-neighbor hopping (NNH),\(^{17}\) and the values of 3 and 4 mean two and three dimensional variable-range hopping (VRH), respectively.\(^{18}\) The value of 2 means Efros VRH.\(^{19,20}\) As shown in Fig. 2(b), the experimental data of the 6.7-Pa film can be expressed by the equation with \(m = 4\). Thus, the carrier transport probably follows three dimensional VRH. On the other hands, naturally, the data of the semimetallic films such as the nonhydrogenated film are not explained by the hopping theories.

Figure 3 shows the X-ray photoelectron spectra of the films. Peaks due to O 1s, C 1s, and B 1s are clearly observed. The boron content was calculated using the following equation.

\[
B/(C + B) = \frac{A_B/I_B}{A_C/I_C + A_B/I_B}
\]

Here, \(A_B\) and \(A_C\) are the total integrated area of C 1s and B 1s peaks, and \(I_B\) and \(I_C\) are the photoionization cross sections for C 1s and B 1s, respectively. The boron contents of the films, that ranges between 3 and 4 at.%, are hardly dependent on the hydrogen pressure. Therefore, the remarkable change in the electrical conductivity with the hydrogen pressure is not attributed to a difference in the boron content in the films.

NEXAFS spectra were measured and analyzed to investigate the origin of the hydrogen-pressure dependent electrical conductivity. Intensities of the spectra were normalized at 330 eV. Figure 4(a) and 4(b) show the C K-edge spectra of the nonhydrogenated and 26.7-Pa films, respectively. A peak due to a C 1s core exciton and a dip profile due to the second band gap, which are typical features of bulk diamond,\(^{21}\) are not observed at 291 and 302 eV in the spectra. This might be because the films comprise UNCD grains with poor crystallinities and contain a certain amount of amorphous carbon.

Features labeled \(A_c\) at 285 eV and \(B_c\) at 286 eV are attributable to \(\pi^*\) states of sp\(^2\)-bonded carbon.\(^{22}\) The nonhydrogenated film seems to have two types of \(\pi^*\) states, and obviously contains more sp\(^2\) bonds than that of the 26.7-Pa film. Atomic hydrogen is well known to preferentially etch sp\(^2\) bonds, which might be a reason for the less sp\(^2\) bonds of the 26.7-Pa film.

A feature labeled \(C_C\) at 289 eV is close to the resonance of \(\sigma^*\)-C–C.\(^{23}\) However, its resonance might not necessarily predominantly contribute to the label \(C_C\), since there are many other resonances around the label \(C\). \(\pi^*\) resonances due to C–B, C=C=O, and C–H bonds occurs at 286.8, 286.5, and 287.5 eV, respectively.\(^{8,24,25}\) C=O bonds should exist on the film surface due to exposure to air. The 26.7-Pa film should contain C–H bonds GBs and an a-C:H matrix in the films.\(^7\) The detailed analysis is under investigation, considering additional results obtained by other spectroscopic methods.

NEXAFS B K-edge spectra of the films are shown in Fig. 5. The B K-edge spectrum is divided into a \(\pi^*\) component ranging from 187 to 194 eV and \(\sigma^*\) component ranging from 196 to 208 eV. A feature labeled \(A_B\) at 190 eV is weakens, whereas a feature labeled \(B_B\) at 192.5 eV becomes obviously peaky for the 26.7-Pa film. The origin of the feature \(A_B\) is unknown. Concerning the feature \(B_B\), since the peak of the feature \(B_B\) is similarly observed for B:C and crystalline boron, its origin might be due to B–B bonds.\(^{26}\) Elsewhere, it has been reported that it is due B–C bonds.\(^{27}\)

A feature labeled \(C_B\) at 194.5 eV is known to be due to boron oxide.\(^{28}\) Peaks of the label \(C_B\) might be due to O atoms adsorbed on the film surface.

4. CONCLUSIONS

Boron-doped UNCD/a-C:H films were deposited at different hydrogen pressures by coaxial arc plasma deposition. The nonhydrogenated film becomes
semimetallic, which might be attributable to the formation of rich-sp² bonds in the film. The electrical conductivity widely decreased with increasing hydrogen pressure, and the 26.7-Pa film exhibited a typical semiconducting behavior whose carrier transport follows VRH. Since the hydrogenation suppresses the formation of sp²-bonds that is a source of carriers, the electrical conductivity might be strongly dependent on the hydrogen pressure. Although the hydrogenation seems to affect the bonding of B from the NEXAFS measurements, it is under investigation.

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